Acta Physica Academiae Scientiarum Hungaricae, Tomus 49 (1—3), pp. 159—166 (1980)

ELLIPSOMETRIC STUDY OF SEMICONDUCTOR — — METAL AND METAL — METAL OXIDE THIN FILMS SYSTEM

By

B. SZÜCS, J. ÁDÁM and P. JAKAB

TUNGSRAM RESEARCH INSTITUTE. H-1340 BUDAPEST, HUNGARY

Absorbing thin films can be characterized by a complex refractive index $\bar{n}_1 = n_1 - ik_1$. The complex refractive index raises several experimental and computational problems: the determination of the extinction coefficient k_1 requires a further, independent parameter, and a further, independent equation. For the determination of the complex refractive index and film thickness (d) on the systems Au/Si, Al/Si, NiO/Ni and thin films of Au, Al and NiO, respectively — the reflectance R was applied as new parameter. The dependence of n_1 and k_1 on d was studied using an idealized and a realistic layer model.

1. Introduction

The refractive index and thickness of non-absorbing thin films can be determined very practically by ellipsometry. Conventional ellipsometric measurements furnish the relative changes of ψ (amplitude ratio) and Δ (phase). Inserting them into the fundamental equations of ellipsometry, n_1 and d can be determined.

Absorbing thin films raise a new problem. The complex refractive index requires the determination of a new unknown quantity k_1. This can be achieved in various ways:

1. To determine every parameter merely by ellipsometry making the measurements with more angles of incidence, substrates, ambient medium, or studying film samples differing in thickness.
2. To combine ellipsometry with other methods, for determining one of the parameters (n_1, k_1 or d) with another (external) measurement, e. g. interferometry, coulometry, rate meter, etc.

The common difficulty of the methods lies in the sophisticated, long, tiresome measurements. The methods are destructive and the results are not unambiguous. A simple, unambiguous solution of the problem was found by applying the PAIK—BOCKRIS (PB) method [1]. By this method, a usual, single ellipsometric measurement provides $\bar{n}_1$ and d simultaneously. This is possible, by choosing the reflectance R as third, independent parameter, beside ψ and Δ. R can be determined with the same measurement by means of the ellipsometer. The two fundamental equations of ellipsometry are to be completed by a third independent equation of reflectance. This experimental and evaluating method is called RPD, i. e. "*r*eflectance-*p*si-*d*elta" method.

The fundamental equation of ellipsometry is:

$$\operatorname{tg}\psi \cdot e^{i\Delta} = \frac{|\bar{r}_p|}{|\bar{r}_n|} e^{i(\delta_p - \delta_n)}, \tag{1}$$

where $\bar{r}_n$ and $\bar{r}_p$, respectively, are the normal and parallel generalized Fresnel reflection coefficients of polarized light, δ_n and δ_p, respectively, denote the phase shifts of the components.

Separating the real and imaginary parts of Eq. (1) gives:

$$\operatorname{tg}\psi = f_1(n_1, k_1 d), \tag{2}$$

$$\Delta = f_2(n_1, k_1, d). \tag{3}$$

A third independent equation would be given by $\bar{r}_p$ or $\bar{r}_n$, however in practice it is more advantageous to use their resultant, the reflectance R. Its equation is [1], [2], [3], [4]

$$R = |\bar{r}|^2 = |\bar{r}_p|^2 \sin^2\alpha + |\bar{r}_n|^2 \cos^2\alpha, \tag{4}$$

denoting by α the azimuth of incident light.

$$R = f_3(n_1, k_1, d). \tag{5}$$

For $\alpha = \pi/4$

$$R = \frac{1}{2}\left(|\bar{r}_p|^2 + |\bar{r}_n|^2\right). \tag{6}$$

By measuring only the relative changes of R instead of its absolute value the disturbing effects of the optical system can be eliminated.

The reflectance can be easily determined by intensity measurement.

Since

$$I_d = K I_i |\bar{r}|^2, \tag{7}$$

where I_d is the intensity of light reaching the detector, I_i is the intensity of light incident on the sample and K is a constant depending on the optical system

$$\frac{I_{dx} - I_{d0}}{I_{d0}} = \frac{\delta I}{I_{d0}} = \frac{2\delta |\bar{r}|}{|\bar{r}_0|} = 2\,\frac{|\bar{r}_x| - |\bar{r}_0|}{|\bar{r}_0|} \tag{8}$$

$$|\bar{r}_x| = |\bar{r}_0| \left(1 - \frac{\delta I}{2 I_{d0}}\right) \tag{9}$$

denoting by I_{d0} the intensity of light reflected by the clean substrate, by I_{dx} the intensity of light reflected by the thin film covered substrate, by $\bar{r}_0$ the reflection coefficient of the clean substrate, by $\bar{r}_x$ the reflection coefficient of the thin film covered substrate and by δI the intensity change due to the covering film.

The intensity was measured with the analyzer position turned by $\pi/2$ with respect to the extinction position.

Measurements were carried out by a usual manually driven ellipsometer set up, operating with the Archer method.

2. Study of stratified planar structures with an idealized and a realistic model

During the preparation and formation of thin films on substrates, considerable deviations may occur between the optical constant of ideal film substrate (Fig. 1) and real oxide film/film/interface/substrate (Fig. 2) systems, due to oxidation or the incorporation of contaminants.

Thus, in practice a real system containing surface and interface layers forms a multilayer structure. The optical parameters of multilayer systems can be calculated by the matrix method.

The effect of surface and interface layers on the optical parameters have been computed with a model, based on the matrix method.

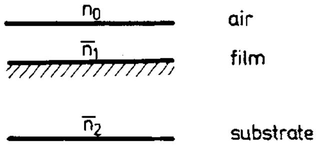

Fig. 1. Idealized (3 component) system

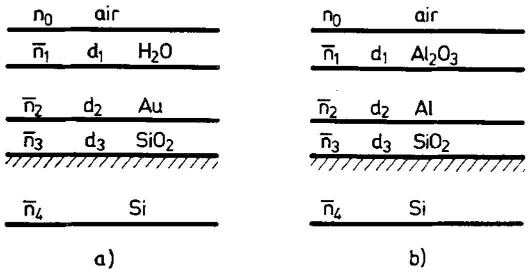

Fig. 2. Real (5 component) system
Optical data: a. $n_1 = 1{,}33$, $n_3 = 1{,}46$, $\bar{n}_4 = 4.05 - i0.028$. Thickness values: $d_1 = 0{,}5$ nm, $d_3 = 2$ nm; b. $n_1 = 1{,}6$, $n_3 = 1{,}46$; $d_1 = 3{,}5$ nm, $d_3 = 3$ nm

Reflection and transmission effects on a boundary can be described by the equation

$$\bar{E}_i = \mathbf{S} . \bar{E}_j \tag{10}$$

according to AZZAM [5], denoting by $\bar{E}_i$ and $\bar{E}_j$ the electric field on the two sides of the boundary. **S** is the scattering matrix.

The latter is formed by the product of matrices representing the effects of interface and those of the layers

$$\mathbf{S} = \mathbf{I}_{01} \mathbf{L}_1 \mathbf{I}_{12} \mathbf{L}_2 \; \dots \; \mathbf{L}_m \mathbf{I}_{m\,(m+1)} . \tag{11}$$

The interface matrix for the i/j boundary is:

$$\mathbf{I}_{ij} = \frac{1}{\bar{t}_{ij}} \begin{bmatrix} 1 & \bar{r}_{ij} \\ \bar{r}_{ij} & 1 \end{bmatrix}; \quad (i = j - 1) \tag{12}$$

denoting by $\bar{t}_{ii}$ the transmission coefficient, and by $\bar{r}_{ij}$ the reflection coefficient.

The layer matrix for the j-th layer is

$$\mathbf{L}_j = \begin{bmatrix} e^{i\bar{\delta}_j} & 0 \\ 0 & e^{i\bar{\delta}_j} \end{bmatrix}, \tag{13}$$

with

$$\bar{\delta}_j = \frac{2\pi}{\lambda_0} d_j \cdot \bar{n}_j \cdot \cos \bar{\varphi}_j ,$$

the phase shift of incident light traversing the layer where λ_0 is the wavelength of incident light and $\bar{\varphi}_j$ is the complex angle of refraction.

The scattering matrix for an arbitrary number of layers is

$$\mathbf{S} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} . \tag{14}$$

The fundamental equation of ellipsometry becomes:

$$\bar{r} = \frac{\bar{r}_p}{\bar{r}_n} = \frac{S_{21p}}{S_{11p}} \cdot \frac{S_{11n}}{S_{21n}} . \tag{15}$$

For our idealized (3 component) system (Fig. 1)

$$\mathbf{S} = \mathbf{I}_{01} \mathbf{L}_1 \mathbf{I}_{12} \tag{16}$$

and for the realistic (5 component) system

$$\mathbf{S} = \mathbf{I}_{01} \mathbf{L}_1 \mathbf{I}_{12} \mathbf{L}_2 \mathbf{I}_{23} \mathbf{L}_3 \mathbf{I}_{34} . \tag{17}$$

An ALGOL program was developed, suitable for computing the thickness and refractive index of the absorbing thin film, taking into consideration the effects of surface oxide film and the interface.

3. Experimental work

Experiments were carried out on Au and Al films, evaporated on Si substrate ($\bar{n}_2 = 4.05 - i0.028$) and NiO films grown by a thermal process on Ni substrate. The variation of the complex refractive index with film thickness was studied.

Type p Si(111) wafers (Wacker, 6 ohm cm) were used. They were etched in 98% H_2SO_4 for 10 min, rinsed in H_2O, dried and annealed in vacuum (5.10^{-5} Pa) at 573 K.

Au was evaporated from a tungsten boat, Al from a tungsten coil, using the following conditions:

substrate temperature: $T_h = 423$ K,
pressure: $p = 5.10^{-4}$ Pa,
deposition rate: $r_{\mathrm{Au}} = 0.4$ nm/s,
$r_{\mathrm{Al}} = 4$ nm/s.

Thermal growth of NiO was made at atmospheric pressure in an oxidizing furnace at 673 K. The NiO films were grown on polished (mechanical) and etched Ni substrates (Vakuumschmelze type S), baked in inert gas. The complex refractive index of the Ni substrate was determined on a great number of samples with the ellipsometer:

$$\bar{n}_2 = 1.731 - i3.26.$$

The thickness of the NiO film was controlled by the oxidation time.

Ellipsometric measurements were carried out with $\lambda = 546.1$ nm polarized light, produced by a stabilized light source. $\varphi_0 = 70°$ was chosen as angle of incidence [1], in order to provide sufficient sensitivity for the $\delta\psi$, δR and $\delta\Delta$ measurements. Considering the principal angles of incidence for Si and Ni ($\varphi_{P\mathrm{Si}} = 76.13°$, $\varphi_{P\mathrm{Ni}} = 79.9°$), ψ, Δ and R can be determined with a reasonable accuracy.

The refractive index and extinction coefficient of Au vs d film thickness are presented in Fig. 3, those of Al in Fig. 4. Curves n_r and k_r represent results calculated by the real, n_i and k_i those calculated by the idealized layer model.

In the case of Au thin film, the deviations between n_r and n_i are significant, according to Fig. 3, whereas the relative differences between k_r and k_i are much lower. For Al thin films, the difference $k_r - k_i$ becomes also sig-

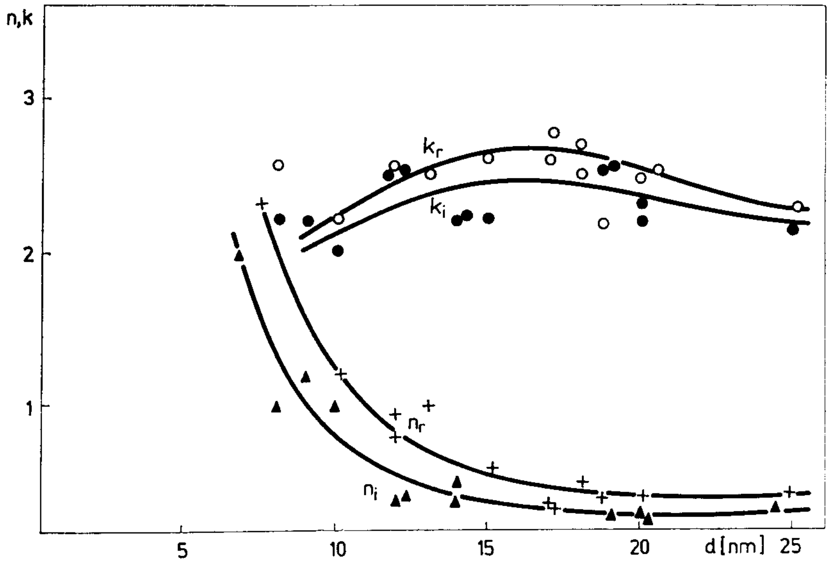

Fig. 3. Thickness dependence of the complex refractive index of Au film on Si substrate for the idealized $[\bar{n}_2 = n_i - ik_i]$ and realistic $[\bar{n}_2 = n_r - ik_r]$ layer models

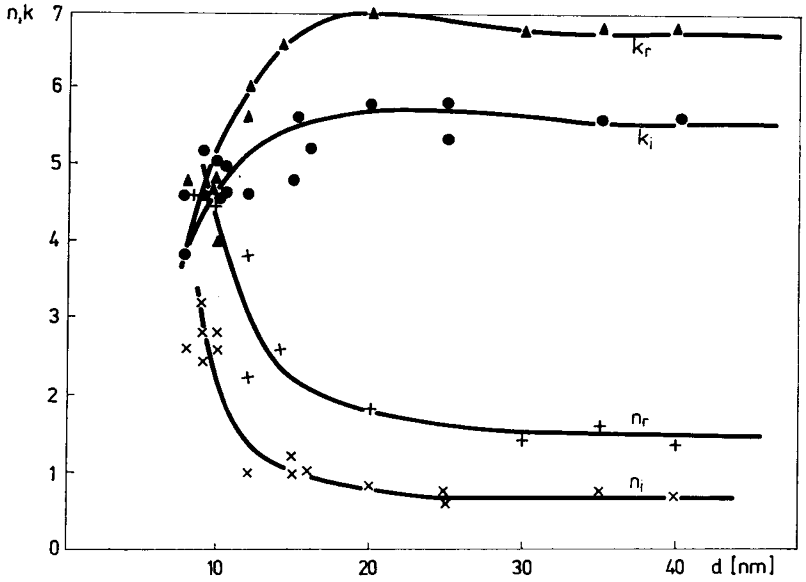

Fig. 4. Thickness dependence of the complex refractive index of Al film on Si substrate for the idealized $[\bar{n}_2 = n_i - ik_i]$ and realistic $[\bar{n}_2 = n_r - ik_r]$ layer models

nificant (Fig. 4). For Au and Al films, it was found that $n_r > n_f$, and $k_r > k_f$. n_1 and k_1 exhibit a strong thickness dependence in the $6 < d < 15$ nm range. Below $d < 6$ nm anomalies were noticed on our samples and layer systems. In this low d range, the application of various approximations (MAXWELL—GARNETT, STRACHAN and SIVUKHIN) did not supply reasonable results for the equivalent n_e, k_e, and d_e.

In the studies of the relations between refractive index and layer structure, the early stages of layer formation before achieving a continuous film, have been checked by electronmicroscopy (at the Research Institute for Technical Physics of the Hungarian Academy of Sciences).

Unambiguous $n_1 - d$, $k_1 - d$ relations were found on Au for $d > 8$ nm, on Al for $d > 6$ nm thickness. Films of $d_e \approx 4$ nm exhibited a granular structure. In the $d \approx 4$—6 nm range, island type structure is characteristic. For Au films above $d_e \approx 7$—8 nm, for Al above $d_e \approx 6$—7 nm, the coalescence of islands is starting. Above 10 nm, the continuous layer structure is built up. The anomalies of n_1 and k_1 can be explained by these structural transformations, and the big changes in the $6 < d < 15$ nm range as well.

The refractive index and extinction coefficient vs film thickness of NiO are presented in Fig. 5. Comparing them with results described in [8], these values are realistic. Comparing the n_r and k_r results with data published in the literature [6], [7] and taking into consideration the conditions of preparation the agreement is good.

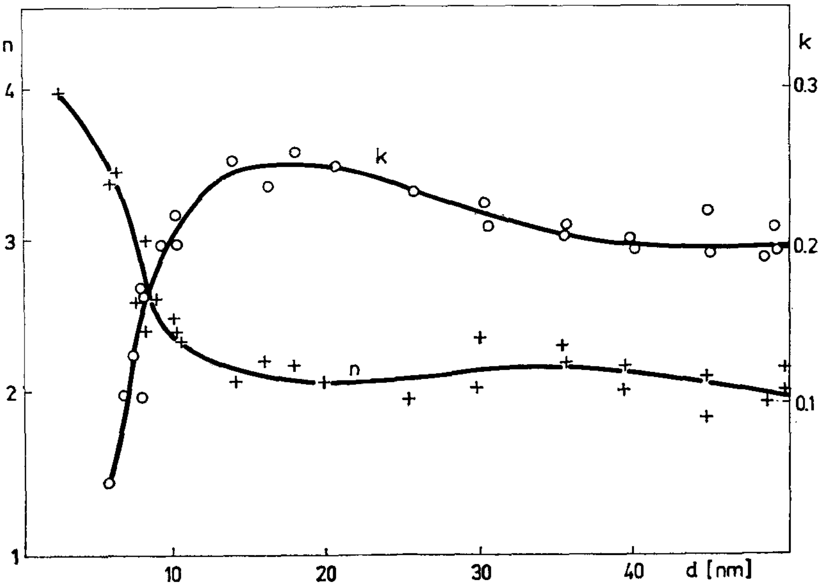

Fig. 5. Thickness dependence of the complex refractive index of NiO film prepared by thermal oxidation of Ni substrate

4. Conclusion

An experimental and computational ellipsometric method was developed for determining the refractive index and thickness of absorbing metal and metal oxide thin films. The RPD method proved to be adequate for evaporated Au and Al films, and NiO films as well, prepared by thermal oxidation.

Acknowledgements

The authors express their sincere thanks to Mr. E. Barla, Director of the Tungsram Research Institute, for supporting their research work, to Dr. Gy. Gergely for his valuable advice in studying the structural dependence of refractive index and to Dr. B. P. Barna (Research Institute for Technical Physics, Hungarian Academy of Sciences). for the electronmicroscopic analysis of our samples.

The authors are indebted to Mrs. M. Várnai for kindly preparing the samples.

REFERENCES

1. W-K. Paik and J. O'M. Bockris, Surface Sci., **28**, 61, 1971.
2. M. Born and E. Wolf, Principles of Optics, Pergamon Press, Oxford, 1965.
3. B. D. Cahan, J. Horkans and E. Yeager, Surface Sci., **37**, 559, 1973.
4. R. C. O'Handley, Surface Sci., **46**, 24, 1974.
5. R. M. A. Azzam and N. M. Bashara, Ellipsometry and Polarized Light, North-Holland Publ. Co., Amsterdam, 1977.
6. O. S. Heavens, Optical Properties of Thin Solid Films, Butterworths Sci. Publ., London, 1955.
7. L. K. Chopra, Thin Film Phenomena, McGraw-Hill Book Company Inc., New York, 1969.
8. K. Gupta, J. P. Marton and J. Shewchun, J. Electrochem. Soc., **121**, 118, 1974.